



Simultaneous production of glyceric acid and hydrogen from the photooxidation of crude glycerol using TiSi_2

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ABSTRACT

The biodiesel industry is facing a problem with glycerol market saturation due to the large amounts of glycerol co-product that are produced during biodiesel processing. This is also having a negative impact on our environment. The crude glycerol obtained from biodiesel industry is at basic pH (~12–14) because of soluble bases such as potassium hydroxide (KOH) or sodium hydroxide (NaOH). In this work, the use of solid photo catalyst, titanium disilicide (TiSi_2) is investigated for glycerol oxidation in basic aqueous solution under mild conditions. The oxidation in a batch reactor at 65 °C and atmospheric pressure using *in situ* oxygen as oxidant showed 100% selectivity toward glyceric acid. Conversion efficiency of glycerol was observed around 64% over 6 h. Higher conversion (97.6%) was also observed over prolonged reaction conditions (~12 h).

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1. Introduction

When biodiesel is produced the primary output other than biodiesel is glycerol (1,2,3-propanetriol). For every 10 kg of biodiesel, approximately 1 kg of glycerol is also produced [1]. Currently, 266 million liters of glycerol is produced annually in the US and 14,896 million liters are produced worldwide [2]. With the advent of biodiesel industry, conversion of glycerol into high value chemicals emerged as a new branch of research [3]. In this aspect, conversion of glycerol to value added product is vital from both economical as well as environmental point of view [4–6].

Glyceric acid (GA) is one of the useful chemicals with medicinal [7–9] and industrial value [10,11] which can be obtained from glycerol oxidation. Glyceric acid (2,3-dihydroxypropionic acid) is naturally found as a phytochemical constituent in a variety of plants, such as peanuts, artichokes, tomatoes, apples, bananas, and grapes [12].

Chemoselective catalytical oxidation of glycerol over metallic catalysts such as platinum, palladium and gold has been shown to be a good technique for obtaining selective oxidative products from glycerol [13–15]. The synthesis of glyceric acid from pure glycerol has been reported by several research groups [16–18] using exter-

nal oxidants. Although glycerol's unique structure makes it possible to conduct the heterogeneous catalytic oxidative reactions using oxidizing agents such as air, oxygen and hydrogen peroxide, the extensive functionalization of the glycerol molecule with hydroxyl groups of similar reactivity renders its selective conversion particularly difficult. Higher glycerol conversions with good selectivity are difficult due to over oxidation [19]. In presence of air (1 bar), under mild conditions (60 °C) Hutchings and coworkers [13] found that glycerol over oxidizes to CO_2 , HCHO and HCOOH however they optimized the conditions using pure oxygen to achieve 100% selectivity to glyceric acid. Prati and coworkers [20] found that bimetallic catalysts are superior to monometallic catalyst. They also showed that the selectivity toward glyceric acid can be improved by changing the reaction conditions. Besson and coworkers successfully performed liquid phase oxidation of glycerol to glyceric acid using Pt/C catalyst under air atmosphere [21]. Addition of boron to this catalyst improved the selectivity from 55% to 70%. Under these reaction conditions they found that this oxidation reaction is limited by the rate of diffusion of oxidants (oxygen) from the gas phase into liquid phase [21]. However, increasing the partial pressures creates additional problems. Catalysts based on the platinum group metal suffer oxygen poisoning proportional to oxygen partial pressure [22,23]. This study focuses to achieve high glyceric acid selectivity under mild photocatalytic conditions. TiSi_2 is selected as the catalyst due to its potential for water splitting reactions under mild conditions [24].

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Demuth and his team explored the possibility of titanium disilicide (TiSi_2) for photocatalytic hydrogen generation by water splitting reaction [25]. TiSi_2 has very unique optoelectronic properties that are ideal for use in solar applications: broad-band reflectance measurements show a band-gap range from 3.4 eV to 1.5 eV for TiSi_2 [25]. As a result, this material absorbs light over a wide range of the solar spectrum (360–800 nm), is easily available and inexpensive. In their work, they also proved TiSi_2 has peculiar surface oxygen storage properties at lower temperatures up to 100 °C.

This paper describes a simple photocatalytic oxidation of aqueous glycerol to glyceric acid by exploiting TiSi_2 oxygen storing properties ~100 °C when used as a photo catalyst [25]. Glycerol oxidation was carried out using the *in situ* generated oxygen from the photocatalytic activity of TiSi_2 at 65 °C under ambient conditions. A mechanism for selective glycerate production is proposed considering the physisorbed oxygen on the TiSi_2 surface.

2. Experimental

2.1. Materials

Glycerol ($\text{C}_3\text{H}_8\text{O}_3$, ACS grade, Fluka, USA), titanium disilicide (TiSi_2 , 99.5% metal basis, Alfa Aesar, USA), potassium hydroxide (KOH, 86%, Sigma–Aldrich, USA), and hydrochloric acid (HCl, ACS reagent grade, Sigma–Aldrich, USA) were used as received. Crude glycerol was obtained from biodiesel production using spent coffee oil, feather meal fat as biodiesel feedstocks as reported in our earlier reported work [26,27].

2.2. Catalyst characterization

Commercially available TiSi_2 was used as a photo catalyst. However, the crystallinity and formation of oxidative products such as TiO_2 and SiO_2 were tested using X-ray diffraction (XRD). All measurements were carried out by using powder diffraction apparatus (Philips automated XRD) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54018 \text{ \AA}$). Data were acquired on a PC using MDI Data scan software and processed using MDI Jade and ICDD PDF minerals data base. A field-emission scanning electron microscope (FESEM, Hitachi S-4700) was used to analyze the composition and distribution of catalyst material before and after the oxidation reaction. The images were taken at an accelerating voltage of 20 kV. Energy dispersive X-ray (EDX) analysis was obtained using an Oxford detector.

2.3. Photocatalytic oxidation experiments

All photocatalytic oxidative experiments were done using a 300 W solar simulator (69911, Newport-Oriel Instruments) as a light source. An optical AM 1.5 filter (Newport) was used to illuminate the 1 Sun intensity (100 mW/cm², measured by thermopile) on the catalyst at 65 °C. The oxidation of glycerol was carried out in a 100 mL round bottom (RB) flask containing 50 mL, 1 M KOH, and 10 wt% solution of aqueous glycerol (5 g) with 1 wt% TiSi_2 (500 mg). The RB flask was kept 15 cm from the light source. Catalytic testing was performed by dispersing TiSi_2 powders in the above solution under atmospheric pressure.

2.4. Product analysis

The oxidation of glycerol was monitored using a high performance liquid chromatography (HPLC, Shimadzu LCsolution-20-AB) with ultraviolet and refractive index detectors. Reactant and products were separated using an Aminex® HPX-87H ion exclusion column (300 mm × 7.8 mm) heated at 40 °C. The eluent used was a solution of H_2SO_4 ($5 \times 10^{-4} \text{ mol L}^{-1}$) at a flow rate of 0.75 mL/min.

Each time, the reaction mixture samples (10 μL) were diluted to 1 mL using the eluent solution and injected through HPLC. A calibration curve was generated using 10 wt% to 2 wt% solutions of glycerol. The terms 'glycerol conversion' and 'glyceric acid normalized selectivity' used here are defined as follows:

$$\begin{aligned} \text{glycerol conversion (wt\%)} \\ = \frac{\text{initial glycerol concentration} - \text{final glycerol concentration}}{\text{initial glycerol concentration}} \\ \times 100 \end{aligned}$$

$$\text{glyceric acid selectivity} = \frac{\text{glyceric acid in products}}{\text{total products formed}} \times 100$$

The glyceric acid formation was further confirmed by FTIR (Bio-rad). The FTIR measurement was performed as follows. First, the reaction mixture (after 12 h) was neutralized with 12 N hydrochloric acid and the reaction mixture was centrifuged. The excess water was removed by distillation. Second, the sample was cooled to ambient temperature and finally, the sample was compressed into self-supporting membrane with KBr to perform FTIR measurements.

The selectivity as well as the purity of glyceric acid was confirmed using carbon nuclear magnetic resonance (¹³C NMR) spectroscopy by analyzing the reaction mixture obtained after 12 h. The spectrum was obtained on a Varian unity plus machine with 11.75 T magnetic strength and operating at 125 MHz (¹³C) in deuterated water (D_2O). Samples of reaction mixture were neutralized with 12 N hydrochloric acid and water was evaporated before adding D_2O .

The evolved gases were analyzed by gas chromatography (GC, Agilent 6890) with thermal conductivity detector (TCD). The molecular sieve 5A column was used for the separation of gases and nitrogen was used as carrier gas. A flow rate of 30 mL/min was used. The oven and detector temperatures were set as 50 °C and 200 °C, respectively.

3. Results and discussion

A HPLC chromatogram of the reaction mixture for a reaction carried out at 65 °C, 1 M KOH, 10 wt% glycerol (5 g in 50 mL) and 1 wt% TiSi_2 for 12 h under air is shown in Fig. 1A and the results are summarized in Fig. 1B. As shown, glyceric acid was the only product observed with a glycerol conversion to glyceric acid to 97.6% with 100% glyceric acid selectivity. Glyceric acid formation was confirmed from ¹³C NMR. Position of each carbon (1–3) and their corresponding chemical shifts are given in Fig. 2. The formation of glyceric acid further confirmed from FTIR analysis (Fig. 3). The most intense and characteristic bands observed for the reaction products were: 1068, 1296, 1554 and 1668 cm^{−1} [28]. The C–O stretching vibration was observed at 1068 cm^{−1}. Glyceric acid also showed an intense band at 1296 cm^{−1} (C–H bending) which corresponds to the coupling of the CH_2 (C–H) and C=O groups. The glyceric acid also had a strong band at 1554 cm^{−1}, which corresponds to the carbonyl, C=O, stretching ($-\text{C}=\text{O}-$) of the organic acid. The peak at 1668 cm^{−1} is from the solvent (H_2O). The effects of base and TiSi_2 are explained later.

3.1. Alkaline oxidation of glycerol to glycerolate

The crude glycerol obtained from biodiesel industry is at a pH of 11–14 due to dissolved KOH (catalyst for the transesterification reaction). Chemo-selective catalytic oxidation of glycerol experiments were reported favorable at a basic pH of 11 [21]. Kishida et al.

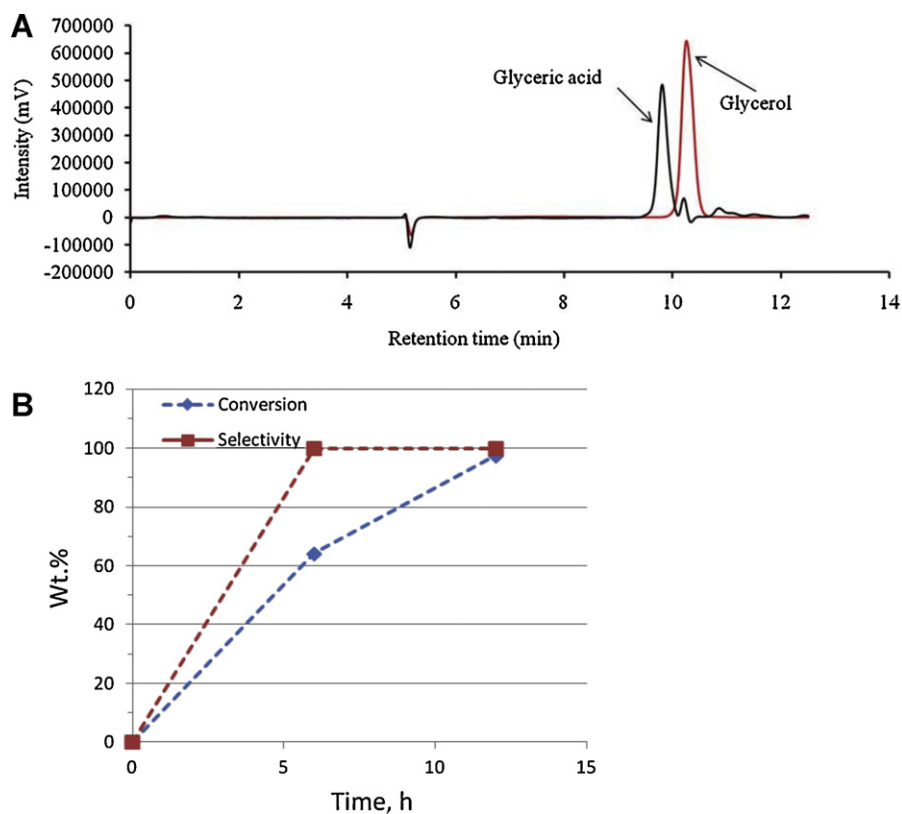


Fig. 1. (A) HPLC chromatogram of pure glycerol and photocatalytic reaction products at 65 °C, 1 M KOH, 10 wt% glycerol (5 g in 50 mL) and 1 wt% TiSi₂. (B) Summary of activity and selectivity obtained from the HPLC analysis.

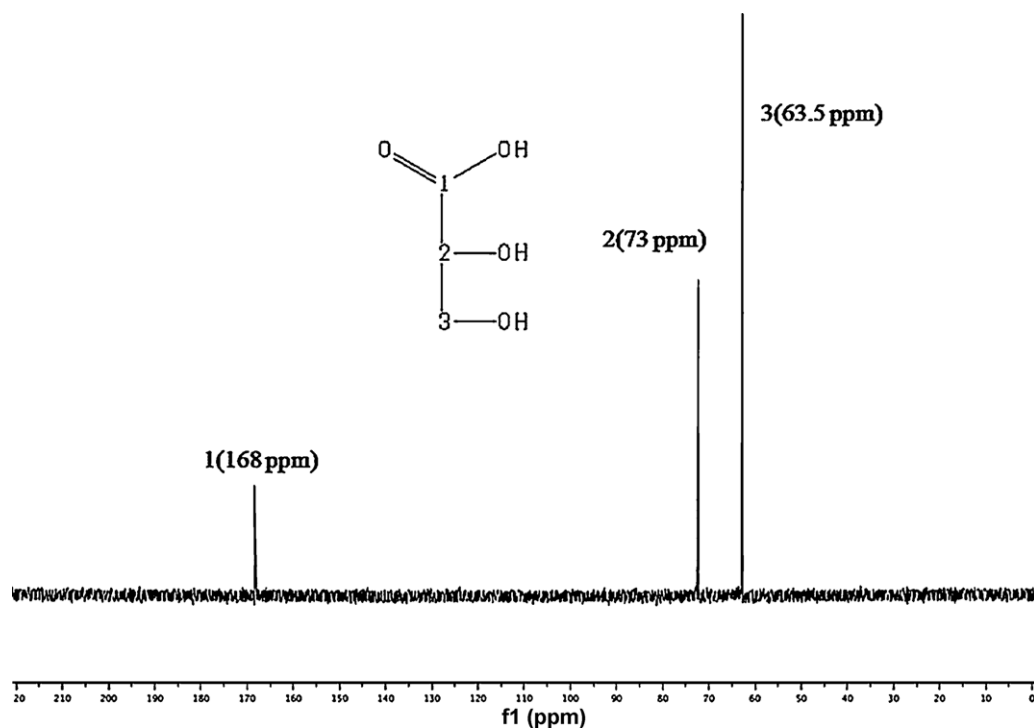


Fig. 2. ¹³C NMR of the reaction end product (glyceric acid) after 12 h of reaction. 97.6% conversion of glycerol to glyceric acid was confirmed.

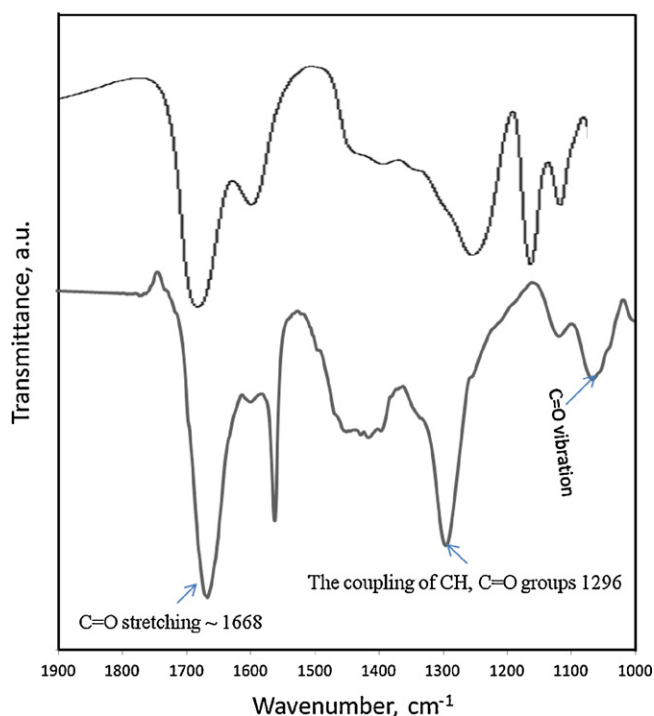
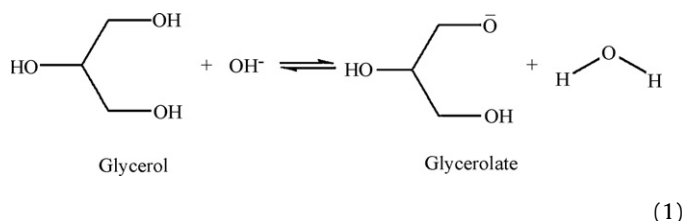


Fig. 3. FTIR spectrum of (a) glyceric acid and (b) reaction end product (glyceric acid) after 12 h.



Water splitting reactions using TiSi_2 as catalyst under sunlight, and its reversible oxygen and hydrogen storage properties were explored thoroughly by Demuth and his research group [25]. They reported that small amounts of hydrogen ($5\text{--}7\text{ mL g}^{-1}$) physisorbed at 50°C when compared to 20 mL g^{-1} , at 30°C . However, the oxygen physisorbed on the TiSi_2 surface remained intact well over 100°C [25]. This result suggests that oxygen can still remain adsorbed by TiSi_2 in presence of light at working temperature (65°C) of this proposed work. At this working temperature, influence of the hydrogen on the oxidation process is neglected as for all practical purposes physisorbed hydrogen amounts on TiSi_2 surface remain low.

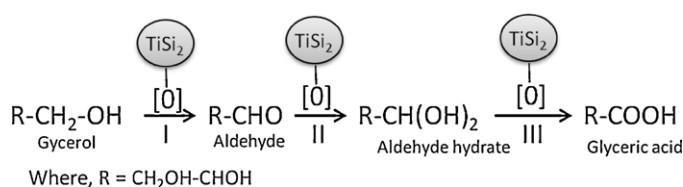


Fig. 4. Proposed reaction sequence of TiSi_2 assisted glycerol oxidation to glyceric acid. Surface stored oxygen of TiSi_2 acts as *in situ* oxidizing agent.

- (i) The rate of oxidation of a primary alcohol function is higher than that of a secondary alcohol.
- (ii) Rapid oxidation of glyceraldehyde favors the formation of surface adsorbed glyceric acid.
- (iii) A basic pH increases desorption of the acid (as potassium salt) from TiSi_2 surface.

When no glycerin and no sodium hydroxide (Eq. (2)) were used the production of hydrogen was reported to be 35 mL/24 h/2000 mg [25].

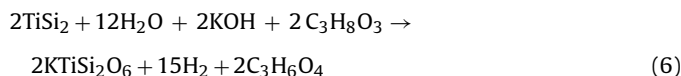


Oxidation of water is the key step for the faster production rates (Eq. (3)). Addition of 1 M KOH helped enhancing the production rate. A higher production rate (10.2 mL/h/50 mg) was observed when 1 M KOH solution (Eq. (5)) was used instead of water. A basic pH increases the oxidation rate of water to oxygen because the deprotonation of the hydroxyl group much easier at higher pHs (Eq. (3)) [32].



However, Ritterskamp et al. [25] reported that, in the hydrogen generation process, the first step is the oxidation of water to oxygen and H^+ ions at the catalytical center (Eq. (2)). But $TiSi_2$ is also a good storage material for thus produced oxygen which adsorbs on the surface of the catalyst material [25]. This might hinder the second step of the process (Eq. (3)) which will be occurred on the surface of the same material ($TiSi_2$). So, removal of the oxygen generated from first step will further enhance the water splitting reaction. Garcia et al. reported that the oxidation of glycerin to glyceric acid reaction limited by the rate of diffusion of oxygen from the gas phase into liquid phase [21].

When a 5 wt% glycerin was used in with the reaction mixture the production of hydrogen increased to 29.4 mL/h/50 mg per hour (Eq. (6)).



This higher production rates attributed to the removal of adsorbed oxygen from surface due to oxidation of glycerin to glyceric acid and making the catalytical sites available for the water oxidation reaction. Contrastingly, the oxygen storage property of titanium disilicide further increases the probability of the glycerol oxidation process at the surface. Thus glycerin oxidation process fastened the water splitting process.

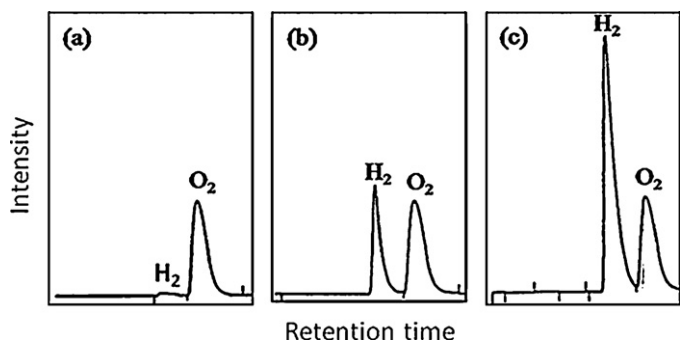


Fig. 5. Gas chromatograms of the gases evolved from the following reactions: (a) water only, (b) 1 M KOH solution and (c) 1 M KOH and 5 wt% glycerin (amount of TiSi_2 , temperature and light intensity were the same for all the above reactions).

3.3. Catalyst stability

TiSi_2 semiconductors are inexpensive and abundant. However, poor stability toward basic water is one disadvantage. Demuth and co-workers reported that the water splitting reaction is not stoichiometric when compared with TiSi_2 , indicating the catalytical nature of the material [25]. However, formation of the passive layers of oxygen impedes the reaction rates. Removal of the adsorbed oxygen using glycerol showed enhancement in the water splitting reaction as shown in Fig. 5. The production of hydrogen is enhanced in the presence of glycerol. All experiments were conducted in ambient conditions, thus, the presence of an oxygen peak is predictable. However, no enhancement of the oxygen peak was observed indicating the oxygen capturing capability of TiSi_2 under working conditions. The presence of glycerol helps scavenge the surface oxygen molecules and promotes the water splitting reaction.

The reaction after 6 h showed only 64.3% glycerol conversion (supporting information) but catalyst was still capable of generating hydrogen. Longer reaction times (12 h) showed 97.6% conversion but the catalyst was not reusable. Fig. 5 shows the scanning electron microscope (SEM) images of (a) TiSi_2 as obtained and (b) after the photo catalytic reaction over 12 h. Though there is no considerable change in the particle size, Energy-dispersive X-ray (EDX) analysis (insert table, Fig. 6) showed the formation of some oxides. Excess oxygen due to the adsorption of KOH or glycerol or glyceric acid is ruled out as the samples were washed and centrifuged several times before the EDX analysis. Formation of crystalline SiO_2 or TiO_2 is also ruled out since the XRD pattern of the sample does not resemble any of those materials (Fig. 7). The disap-

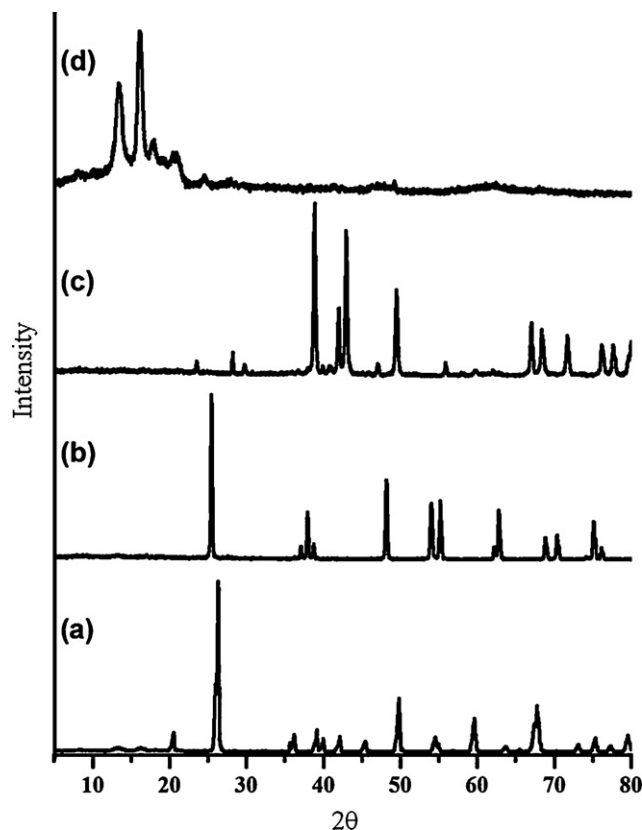


Fig. 7. XRD pattern of (a) SiO_2 , (b) TiO_2 , (c) TiSi_2 and (d) TiSi_2 after 12 h photocatalytic reaction.

pearance of TiSi_2 peaks in the used catalyst may be attributed to the poisoning of the catalyst material in basic medium. The new peaks were not able to match to the XRD library, which needs further investigation. Further, heat treatment of the catalyst sample before XRD measurement was not carried out to retain the chemical structure of as obtained catalyst after the reaction. However by combining the EDX analysis results and Eq. (6) it can be concluded that the TiSi_2 structure converted to pyroxene [33] structured KTiSi_2O_6 complex. Prolonged oxidation in water formed amorphous material from TiSi_2 . However, the need to maintain an optimum concentration of glycerol in the reaction mixture to hinder the catalyst degradation should be explored further.

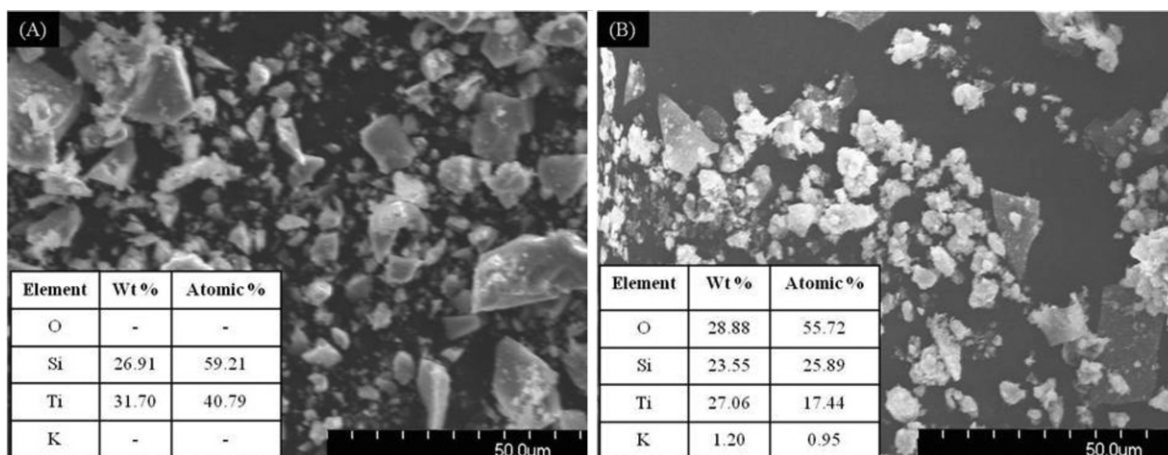


Fig. 6. SEM images of catalyst (TiSi_2) before (A) and after (B) the photocatalysis. EDX analysis (insert table) shows the excess oxygen present in the catalyst after 12 h reaction.

3.4. Crude glycerol and purified glycerol

Crude glycerol was obtained from biodiesel production using spent coffee oil and feathermeal fat as biodiesel feedstocks as reported in our earlier reported work [26,27]. The crude glycerol contained excess methanol, KOH (~ 2 M) and other impurities. Centrifugation separates any solid soap like impurities. However, methanol interference with glyceric acid is ruled out because esterification of acid in presence of base and water cannot proceed efficiently. A maximum glycerol conversion of 96.1% with 100% glyceric acid selectivity was obtained after 12 h of reaction. The results revealed the catalyst is active for even crude glycerol oxidation as well. Further optimization studies are in progress to investigate the correlation between the catalyst properties and selectivity over glyceric acid.

4. Conclusion

This study shows that TiSi_2 can be conveniently employed to selectively oxidize glycerol to glyceric acid using solar light, under mild conditions. 97.6% conversion with 100% selectivity to glyceric acid was obtained after 12 h of reaction at 65°C . The presence of glycerol in aqueous solution helped TiSi_2 in its water splitting reaction and in the formation of glyceric acid. Under these reaction conditions, hydrogen and oxygen are also obtained as value products. However, replacing the batch reaction with the continuous (flow of glycerol) reaction and its effect on preventing the deterioration of the catalyst (TiSi_2) is still needed to be explored. The effects of reaction parameters, particle size of TiSi_2 on product selectivity will also be the subject of further study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.05.006>.

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